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AIR QUALITY MARATHON

Annual Report 1975



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AIR QUALITY
MARATHON

ANNUAL REPORT, 1975

H. D. Griffin
Chief, Air Quality Assessment

TECHNICAL SUPPORT SECTION
NORTHWESTERN REGION
ONTARIO MINISTRY OF THE ENVIRONMENT

July, 1976

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SUMMARY

Air quality investigations by Ontario Ministry of the Environment began in Marathon in mid-1974. Assessment surveys have included ambient air monitoring and vegetation, soil and snow sampling programs. The major industrial source of air pollution is a kraft pulp mill and mercury-cell chlor-alkali chemical plant operated by American Can of Canada Limited.

The initial vegetation and soil survey in August, 1975, showed that sulphur dioxide injury to sensitive vegetation had occurred near the kraft mill. Levels of sulphur and sodium were elevated in both vegetation and soil near the mill and decreased with distance from the source. Mercury concentrations were also excessive in soils near the chemical plant. Computer-prepared contour maps, based on a detailed soil survey in November, clearly indicated the influence of local topography and prevailing wind on airborne deposition of mercury emissions from the chemical plant.

Snow sampling yielded results in agreement with those from vegetation and soil assessment studies. Levels of calcium, chloride, mercury, sodium and sulphate were all elevated near the kraft mill-chemical plant area. Of these contaminants, only sodium and sulphate were generally found at above-background concentrations in snow in the town area nearby.

Dustfall attributable to kraft mill emissions was not high at any of the four monitoring stations in Marathon. Low sulphation rates were also recorded at the same locations, indicating that gaseous sulphur-containing air pollutants were generally absent from the town area.

INTRODUCTION

In 1974, Ontario Ministry of the Environment began air quality investigations in Marathon to assess the effects of operations at American Can of Canada Limited on the area near the Company's mill and in the adjoining townsite to the east. The Company operates a 500 ton per day bleached kraft pulp mill and a chemical plant utilizing a mercury-cell process to manufacture about 35-40 tons per day of chlorine and sodium hydroxide. The kraft mill began production in 1946 and the chemical plant was added in 1952. Potential air contaminants from the pulp mill include sulphur dioxide, soot, fly-ash and other particulate matter from power boilers; hydrogen sulphide, other gaseous organic sulphides, sodium sulphate and sodium carbonate from the chemical recovery process; sodium and calcium salts from the lime kiln; and chlorine and chlorine dioxide from the bleaching operation. Chlorine and mercury could also be emitted from the chemical plant. Minor additional sources would include sawdust from chip piles and dust stirred up by the movement of heavy trucks and other equipment.

Air quality monitoring began in August, 1974, with the installation of dustfall jars and sulphation plates at four sites. A fifth sulphation plate station was added in late 1975. To determine the kind, amount and distribution of contaminants near the American Can mill, a snow sampling survey was conducted in early 1975. A preliminary vegetation and soil assessment study was carried out in August, and this was followed in November with more intensive soil sampling to establish the severity and extent of mercury contamination near the chemical plant.

VEGETATION AND SOIL SAMPLING

(a) August Survey

On August 5-6, the area near the kraft mill was inspected for indications of deposition of particulate matter. Local vegetation was also examined for symptoms of injury caused by air pollutants,

disease and insects. Heavy deposits of grey-white particulate matter were seen on the ground and on grassy vegetation to the south and southwest of the kraft mill. Typical symptoms of acute sulphur dioxide injury were observed on leaves of trembling aspen, mountain ash and red elderberry in a narrow band on the hillside to the northwest of the mill. Injury was rated as trace to moderate (0-5 and 15-35 percent, respectively, of leaf area affected) over a small area of about 0.5 hectares. A larger sulphur dioxide injury zone of about 1.25 hectares was encountered south of the mill (Figure 1). Injury symptoms were observed on foliage of trembling aspen, white birch, speckled alder, willow, viburnum, dogwood, mountain ash, red elderberry and fireweed. No visible effects were noted on black spruce, balsam fir, mountain maple, wild sarsaparilla, wild lily-of-the-valley or bunchberry. Injury, where present, was mostly classed as severe (more than 35 percent of leaf area affected) and the transition from severely damaged to injury-free vegetation was abrupt. The distribution of symptoms suggested that the gas was concentrated near the ground at the leading edge of the injury zone, then drifted higher to affect only the upper parts of mature trees toward the rear of the affected area. Emissions from a power boiler fueled with high-sulphur coal were indicated as the cause of the vegetation injury.

Concentrations of chloride, mercury, sodium and sulphur found in vegetation and soil are summarized in Table 1. Chloride was moderately elevated in trembling aspen at site 5 and decreased at the more distant sites. The foliar content of mercury was elevated at locations 5 and 8. Mercury contamination at the former was attributed to air emissions from the chemical plant and at the latter to spillage of mercury in the vicinity of the Company's stores warehouse area. The chemical plant was indicated as the source of airborne mercury contamination of soils at sites 1 to 4. Mercury in soil at site 8 (and perhaps 7) was ascribed to local deposition of mercury-laden waste. Sodium content of both vegetation and soil was significantly elevated at points near the mill and there was a general gradient of decreasing

sodium concentrations in soil with increasing distance from the source. A similar gradient was evident for sulphur content in vegetation and soil. Increased sulphur concentration in vegetation could have arisen through deposition of sulphur-containing particulate matter or by absorption of sulphur dioxide.

(b) November Survey

To more clearly define the distribution of mercury in soil, a 29-site survey was carried out on November 4-5 (Figure 2). All material was sampled in triplicate and analysed twice. Results were summarized in tabular form (Table 2) and as contour maps (Figures 3 and 4). The latter were derived from a SYMAP computer program developed by Harvard University. The soil contour maps indicate a pattern of mercury distribution influenced by local topography and prevailing wind. Excessive mercury levels (the highest recorded in Ontario soils) were found near the chemical plant. Except for a very minor contribution from mercury in coal fly-ash (about 2 ppm mercury, dry weight) blown onto nearby soil during furnace cleaning operations, soil contamination was attributed to airborne emissions from the chemical plant. The occurrence of heavily contaminated soil to the south of the plant suggests that, with southerly winds, substantial amounts of mercury might be deposited directly onto Lake Superior. Contaminated soil extended to the oil tank area to the northwest, up the hillside to the west and southwest and up to the saddle to the south. All soils drain directly into Lake Superior. Surface soil contained far more mercury than subsurface soil. Evidence of mercury contamination was again found in soil at two remote locations (sites 24 and 27) and in both cases, the source was not attributed to airborne emissions from the chemical plant.

SNOW SAMPLING

Three sets of snow samples from 14 sites in Marathon were obtained in January, February and March, 1975. Results from these surveys, reported earlier, showed that levels of calcium, mercury,

sodium and sulphate were high near the kraft mill area and decreased with distance. Calcium contamination was attributed principally to lime kiln emissions. Elevated levels of sodium and sulphate extended into the town area. Chloride concentration was high only at the sample point closest to the source.

At the six closest sampling sites, visible, grey-coloured, particulate material was observed on the snow surface and in banded, subsurface layers. The maximum extent of visible particulate in snow was about 500 metres from the mill.

AIR MONITORING

(a) Dustfall

Dustfall is one of the most visible classes of air pollutants. It comprises particulate matter which settles out from the atmosphere under the influence of gravity. It is measured by exposing open-top vessels for 30 days and weighing the collected matter. Results are expressed in tons per square mile per month.

The 1975 dustfall sampling sites are shown in Figure 5 and results summarized in Table 3. The monthly criterion was frequently exceeded at only one station (63028), where dust loading was ascribed to dust stirred up from a nearby parking area to the southeast and to sawdust blown in from the wood storage area to the west and northwest. Dustfall which could be attributed to kraft mill emissions did not appear to contribute significantly to amounts measured at any site. Results for the latter part of 1974 showed a similar trend, with dustfall averaging 16, 36, 10 and 14 tons for stations 63027, 63028, 63029 and 63030, respectively.

(b) Sulphation

Sulphation rate is measured by exposing lead dioxide plates to the air for 30-day periods. Lead dioxide reacts with sulphur compounds in the atmosphere to form lead sulphate. Results are expressed in milligrams of sulphur trioxide per hundred square centimetres per day ($\text{mg SO}_3/100 \text{ cm}^2/\text{day}$). Because of its oxidizing power, lead

dioxide converts other reactive sulphur compounds, such as hydrogen sulphide and mercaptans, into sulphate. In Marathon, sulphation rates would therefore represent effects of the presence of both sulphur dioxide and organic sulphides (principally hydrogen sulphide).

Sulphation monitoring sites (Figure 5) yielded the values in Table 3. Sulphation rates were low at all stations and well below the Ontario criterion. In December, a fifth station was added closer to the mill (station 63031) which should record rates higher than those at other locations in Marathon.

ACKNOWLEDGEMENTS

Contributions and assistance from the following agencies is gratefully acknowledged:

- Air Quality Laboratory, Laboratory Branch, for chemical analysis of vegetation and soil samples and for preparing and analysing sulphation plates.
- Inorganic Trace Contaminant Section, Laboratory Branch, for mercury analysis of soil and snow meltwater.
- Regional Laboratory, Northwestern Region, for dustfall weight determinations and for chemical analysis of snow meltwater.
- Phytotoxicology Section, Air Resources Branch, for technical advice, for preparing computer SYMAPS and for processing vegetation and soil samples.
- Water Resources Assessment Unit, Northwestern Region, for assistance in obtaining snow samples.

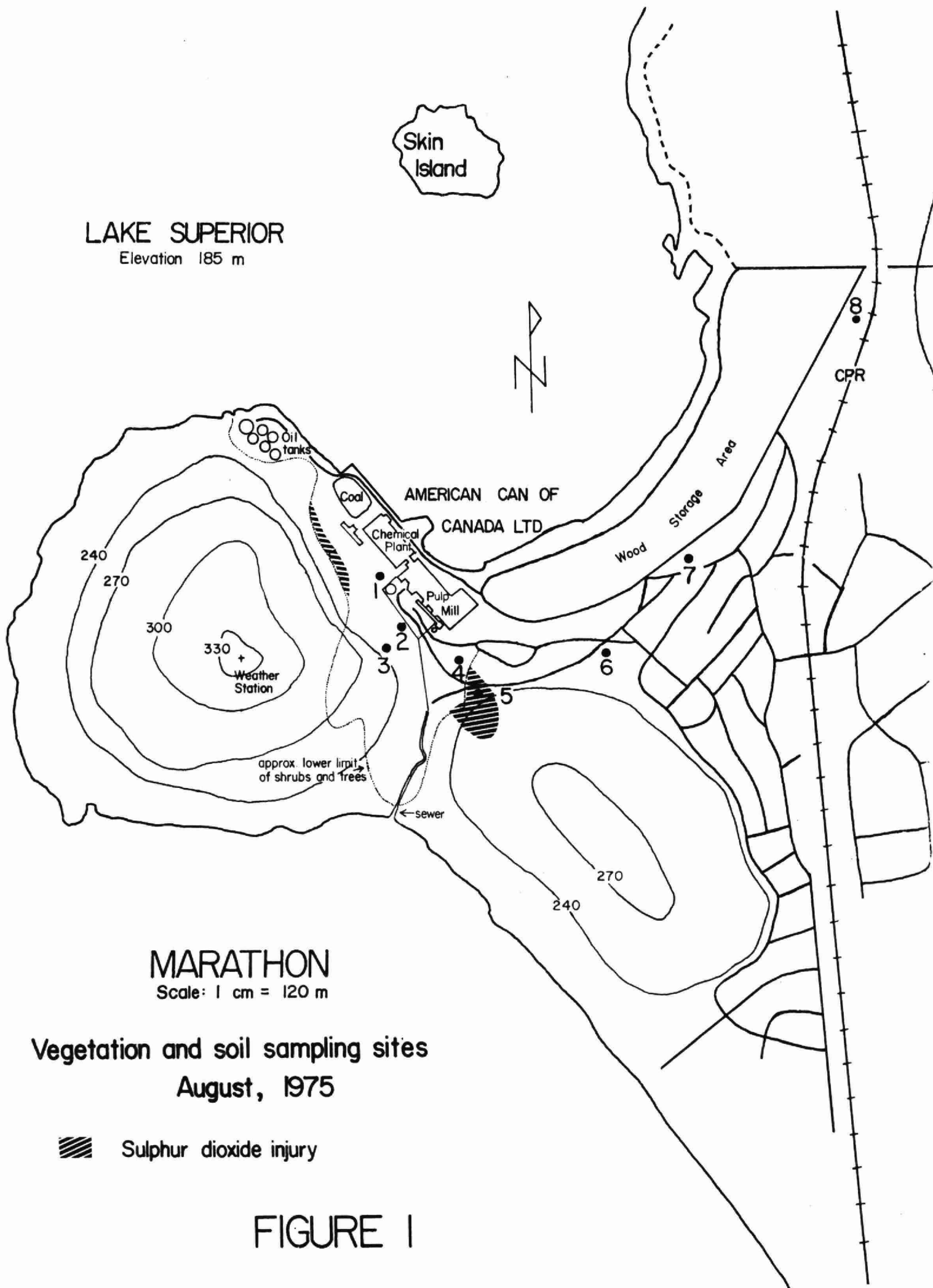
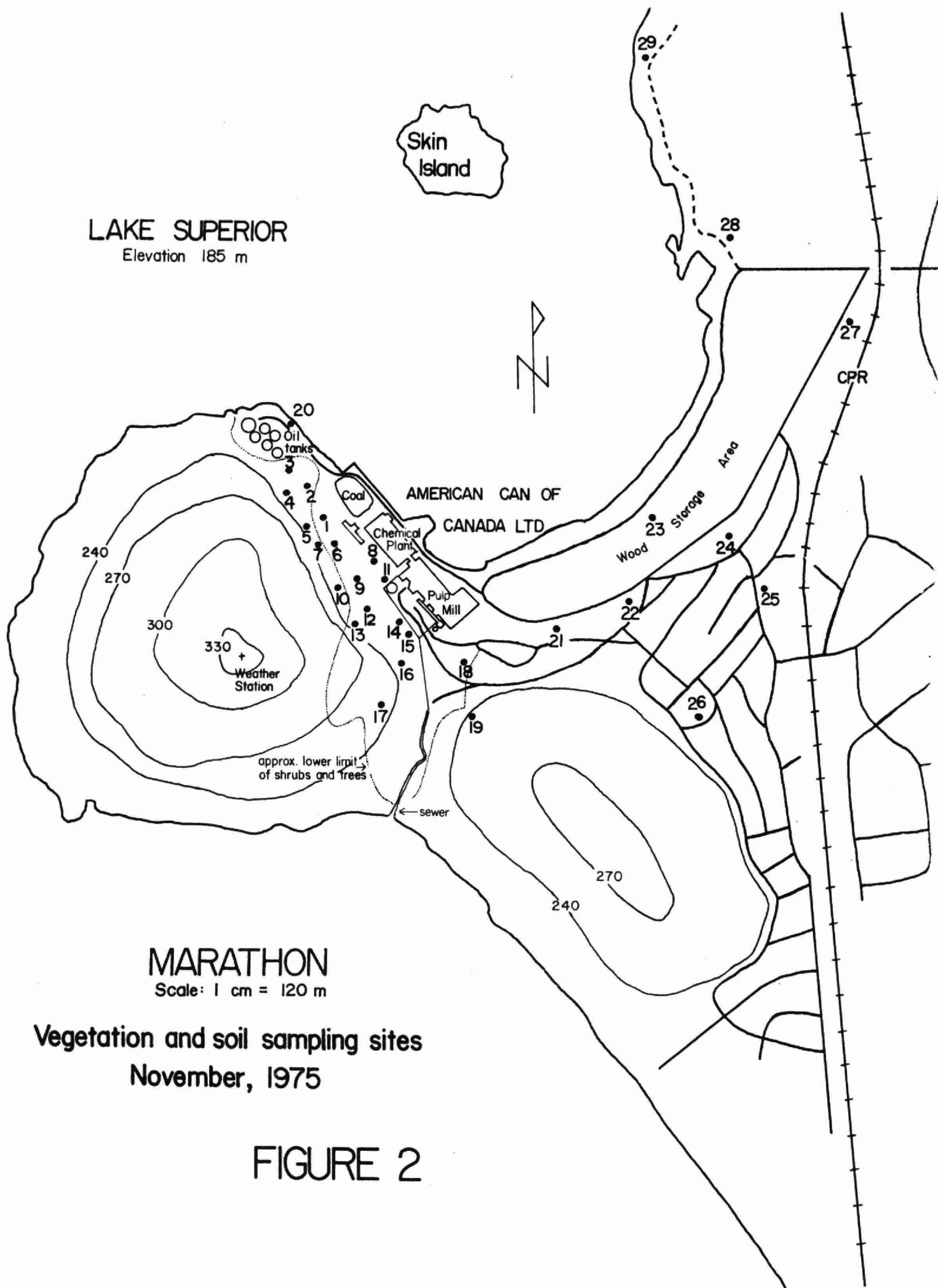


FIGURE 1



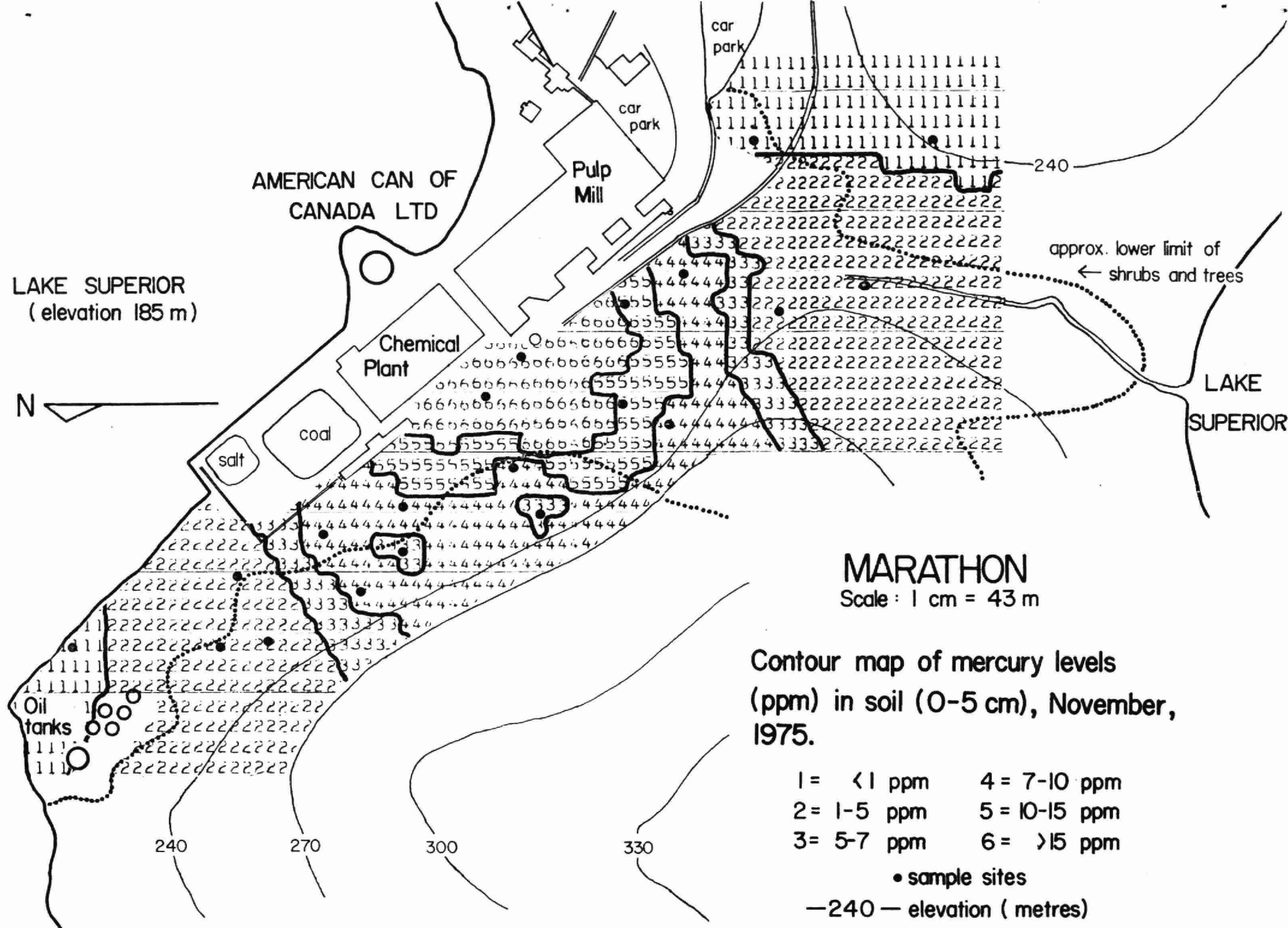


FIGURE 3

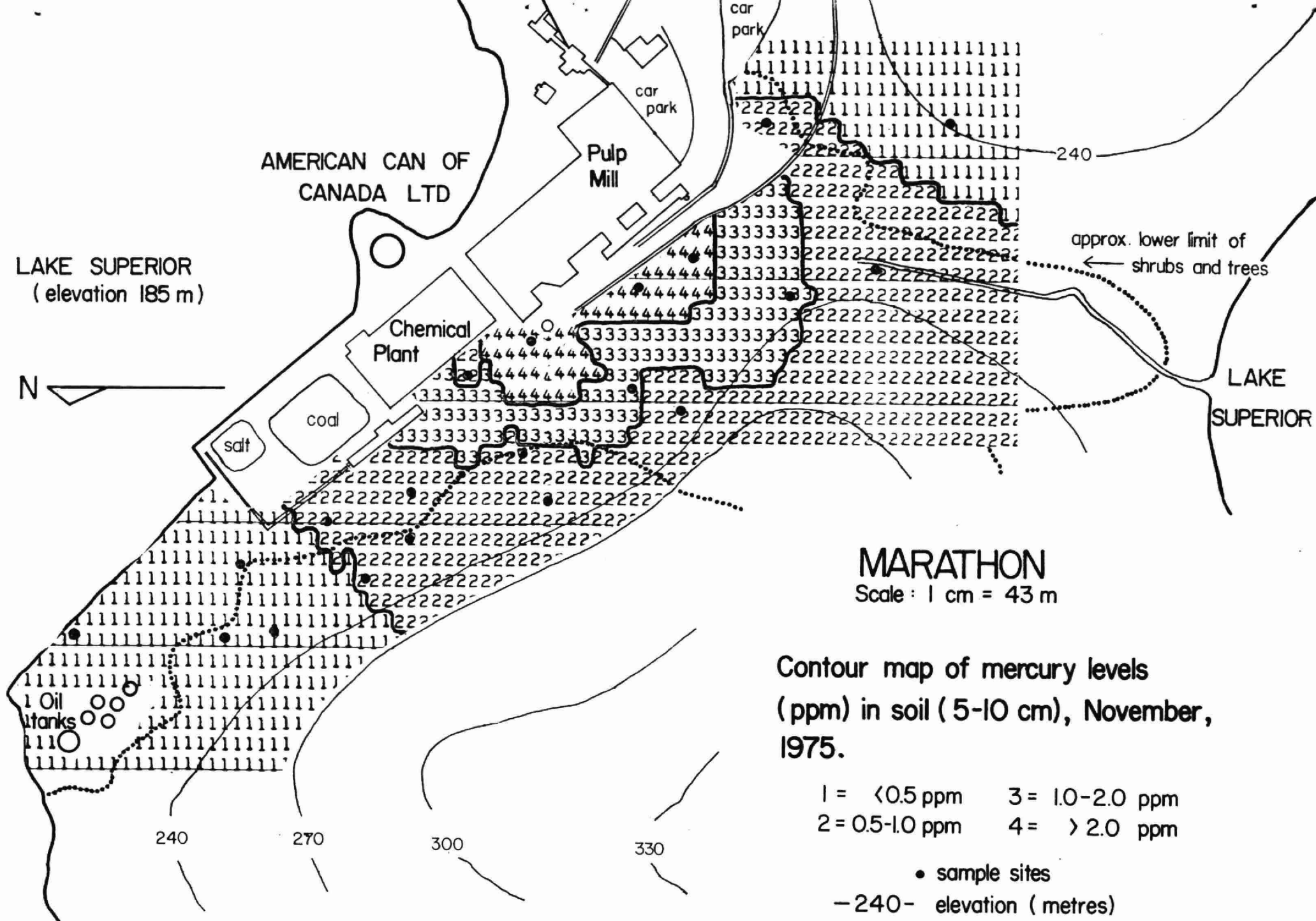


FIGURE 4

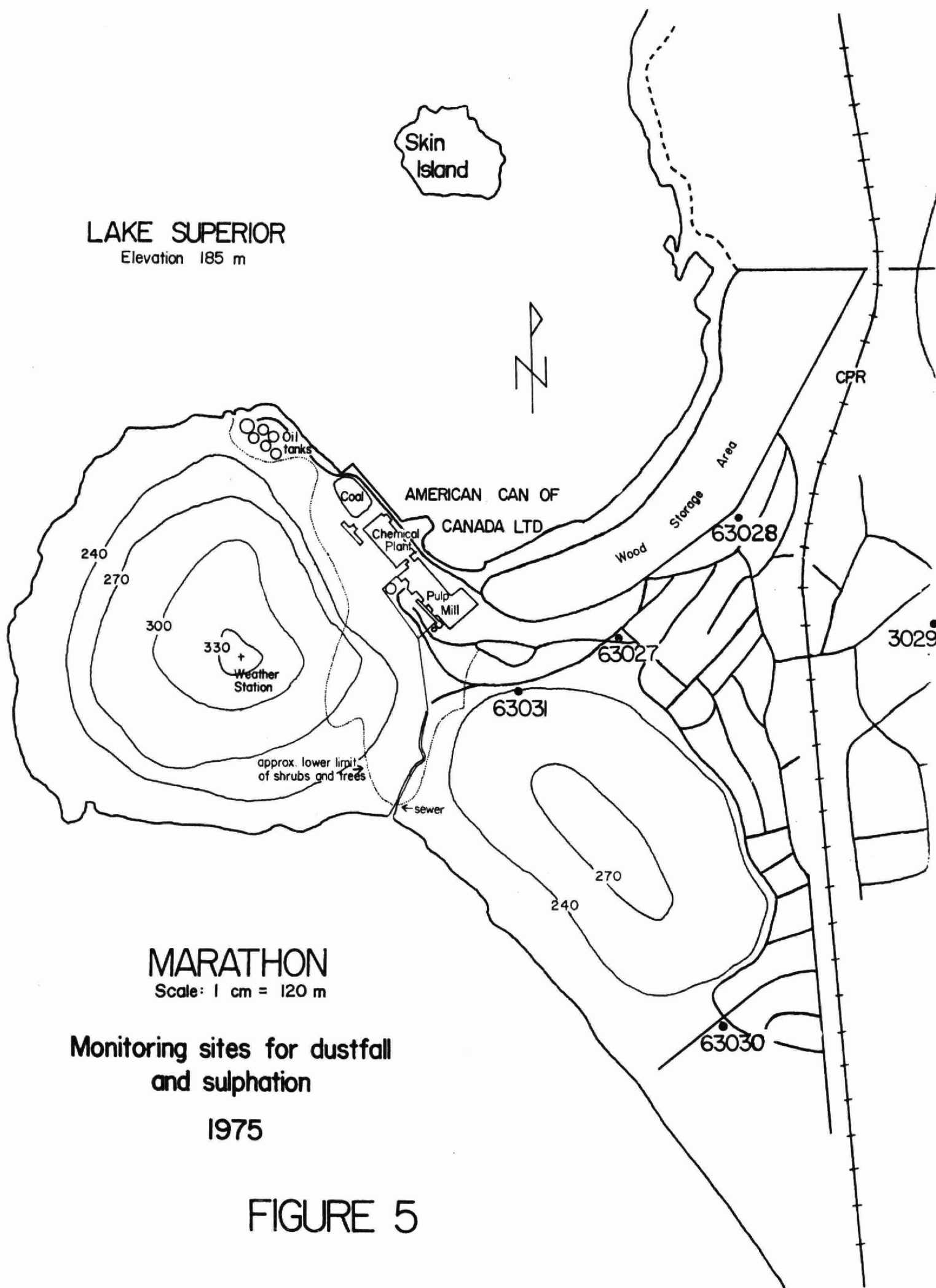


TABLE 1. Levels* of chloride, mercury, sodium and sulphur in not washed trembling aspen foliage and soil, Marathon, August, 1975.

Site	Distance(metres) and direction from source [†]	Trembling aspen				Soil			
						Hg		Na	S
		Cl	Hg	Na	S	0-5 cm	5-10 cm	0-10 cm	
1	70 S					26.6	21.2	1160	0.46
2	205 SSE					4.4	3.9	2130	0.63
3	265 S					4.5	1.1	945	0.39
4	350 SE					0.8	0.6	340	0.15
5	455 SE	0.23	0.42	2415	0.63	0.2	0.1	295	0.12
6	650 ESE	0.15	0.14	202	0.30	0.1	<0.1	159	0.06
7	790 E	0.12	0.15	293	0.22	1.3	1.2	265	0.12
8	1360 ENE	0.12	0.59	228	0.32	1.8	0.4	219	0.16
2500 NE (control)		0.09	<.05	-	-	<0.1	<0.1	95	0.05
5400 NE (control)		0.06	<.05	60	0.22	<0.1	<0.1	72	0.04

*Averages of triplicate samples expressed in percent, dry weight for chloride and sulphur, and parts per million (ppm), dry weight for mercury and sodium.

[†]Source designated as centre of southwest wall of chemical plant.

TABLE 2. Levels* of mercury in soil collected near American Can of Canada Limited, Marathon, November, 1975.

Site	Distance (metres) and direction from centre of southwest wall of chemical plant	Soil depth	
		0-5 cm	5-10 cm
1	170 WNW	7.7	0.5
2	250 NW	2.0	0.4
3	315 NW	3.8	0.4
4	285 WNW	2.6	0.3
5	200 WNW	7.4	0.5
6	120 W	9.1	0.9
7	160 W	6.8	0.5
8	50 SSW	15.6	0.7
9	105 SW	7.8	1.4
10	160 SW	6.9	0.6
11	90 SSE	88.6	12.4
12	170 S	14.5	1.9
13	220 SSW	8.2	0.6
14	190 SSE	10.4	6.9
15	245 SSE	7.9	2.1
16	315 S	3.7	0.8
17	420 S	2.5	0.6
18	355 SE	0.5	0.4
19	500 SSE	0.7	0.3
20	400 NW	0.4	0.2
21	505 ESE	0.2	0.1
22	660 ESE	0.2	0.1
23	720 E	0.2	0.2
24	910 E	0.7	0.2
25	1020 E	0.3	0.3
26	930 ESE	0.4	0.3
27	1360 ENE	1.7	0.2
28	1200 NE	0.4	0.2
29	1430 NNE	0.1	0.1
30	2500 NE (control)	0.2	0.1
31	5400 NE (control)	0.2	0.1

* Parts per million

TABLE 3. Dustfall levels and sulphation rates in Marathon, 1975.

Station	Location	Distance (metres) and direction from source*	Dustfall (tons/square mile/30 days)												Mean
			Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	
63027	McLeod/Abrams	590 ESE	9	6	7	6	<u>25</u>	<u>26</u>	18	18	12	17	8	8	13
63028	Winton/Stevens	875 E	13	8	31 ⁺	-	-	<u>40</u>	59	8	54	<u>43</u>	13	<u>35</u>	<u>30</u>
63029	Marathon Shell	1390 E	4	4	<u>3</u>	8	14	<u>12</u>	<u>7</u>	7	<u>28</u>	<u>13</u>	10	<u>2</u>	<u>9</u>
63030	Howe/Yawkey	1390 SE	4	12	6	11	-	-	12	15	<u>16</u>	16	13	8	11
Sulphation rate (mg SO ₃ /100 cm ² /day)															
63027	McLeod/Abrams	590 ESE	-	.08	.09	.07	.05	.05	.03	.06	.04	.09	-	.13	.07
63028	Winton/Stevens	875 E	.09	.08	.07	.12	.05	.05	.06	.04	.04	.05	.07	.10	.07
63029	Marathon Shell	1390 E	.10	.06	.07	.06	.03	.07	.03	.04	.03	.03	.05	.12	.06
63030	Howe/Yawkey	1390 SE	.15	.20	.13	.07	.03	.03	.04	.04	.04	.04	.09	.16	.09

* Source designated as recovery furnace stack, American Can of Canada Limited.

⁺ Values exceeding criteria of 20 (monthly) or 13 (annual) are underlined.

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